

UNIVERSITY OF WOLLONGONG

DOCTORAL THESIS

Thesis Title

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in the

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Chemistry Department

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Declaration of Authorship

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Date:

"Thanks to my solid academic training, today I can write hundreds of words on virtually any topic without possessing a shred of information, which is how I got a good job in journalism."

Dave Barry

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Chapter 1

Introduction and Literature Review

1.1 The atmosphere

The atmosphere is made up of gases held to the earth's surface by gravity. These gases undergo transport on all scales, from barbecue smoke being blown about the garden, to smoke plumes from forest fires travelling across the world and depositing in the Antarctic snow. They take part in innumerable chemical reactions along the way, largely driven by solar input and interactions with each other. Many gases are lofted into the atmosphere by soil, trees, factories, cars, seas and oceans. They are also deposited back to the surface both directly and in rainfall.

The atmosphere is made up of nitrogen (N_2 : $\sim 78\%$), oxygen (O_2 : $\sim 21\%$), and argon (Ar : $\sim 1\%$), along with water (H_2O) and *trace gases* (those that make up less than 1% of the atmosphere). Water (H_2O) ranges from 0.001 to 1% depending on evaporation and precipitation. Beyond these major constituents the atmosphere has a vast number of trace gases, including carbon dioxide (CO_2 : $\sim 0.4\%$), ozone (O_3 : .000001 to 0.001%), and methane (CH_4 : $\sim 0.4\%$) (Brasseur and Jacob 2017, Ch. 2). Trace gases in the atmosphere can have a large impact on living conditions. They react in complex ways with other elements (anthropogenic and natural), affecting all surface ecosystems upon which life depends.

One important trace gas is ozone (O_3), which affects climate, human health, and ecosystem productivity. This thesis will focus on ozone in the troposphere, which is relatively uncertain over Australia.

Ozone in the lower atmosphere is a serious hazard that causes health problems (Hsieh and Liao 2013), damages agricultural crops worth billions of dollars (Avnery et al. 2013; Yue et al. 2017), and increases the rate of climate warming (Myhre and Shindell 2013). Around 5 to 20 percent of all air pollution related deaths are due to ozone (Monks et al. 2015), roughly .8 million deaths per year (Lelieveld et al. 2013). In the short term, ozone concentrations of ~ 50 - 60 ppbv over eight hours or ~ 80 ppbv over one hour are agreed to constitute a human health hazard (Ayers and Simpson 2006; Lelieveld et al. 2009). Long term exposure causes problems with crop loss and ecosystem damage (Ashmore, Emberson, and Murray Frank 2003), and concentrations may get worse in the future (Lelieveld et al. 2009; Stevenson et al. 2013). Further tropospheric ozone enhancements are projected to drive reductions in global crop yields equivalent to losses of up to \$USD₂₀₀₀ 35 billion per year by 2030 (Avnery et al. 2013), along with detrimental health outcomes equivalent to \sim \$USD₂₀₀₀11.8 billion per year

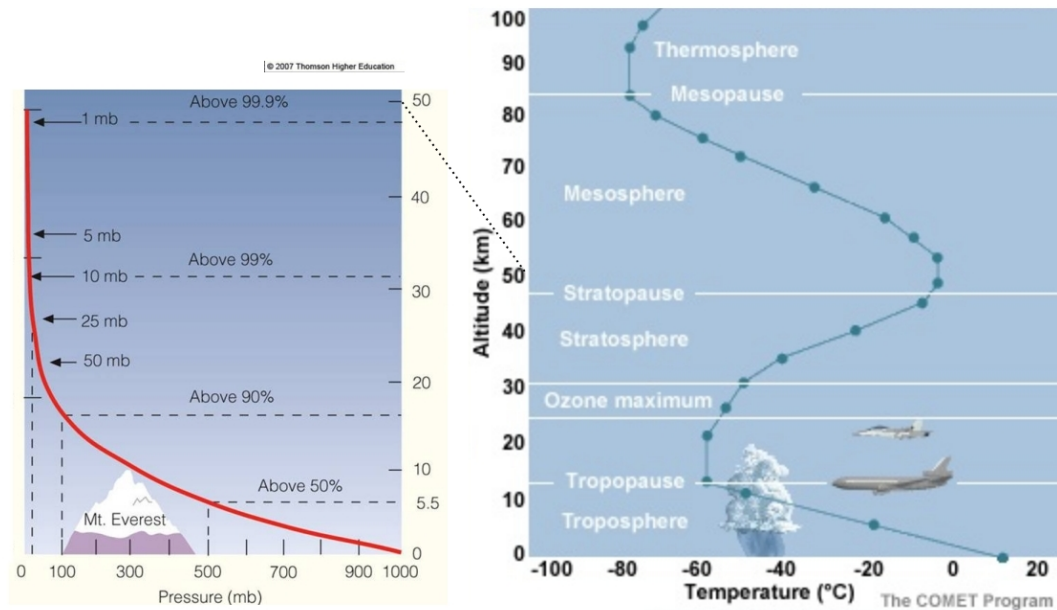


FIGURE 1.1: Pressure (red) logarithmically decreasing, shown with percentage of atmosphere below at several points. Temperature (green) changes throughout the atmosphere. Figure edited from <https://climate.ncsu.edu/edu/Structure>.

by 2050 (Selin et al. 2009). Recently Yue et al. (2017) showed that the net effect of near-surface ozone on is a $\sim 14\%$ decrease in net primary productivity in China. They state that reducing this decrease by $\sim 70\%$ before 2030 would require drastic measures.

1.1.1 Structure

Most of the atmosphere ($\sim 85\%$) is within 10 km of the earth's surface. This is due to air pressure, which decreases logarithmically with altitude. Any entity is subjected to the weight of all the air above it, and the density of the atmosphere is driven by this pressure.

The atmosphere extends above the earth's surface to the edges of space. This is split into various layers, defined by the *lapse rate*: the decrease in temperature (T) with increasing altitude (z), or $-\frac{dT}{dz}$. Figure 1.1 shows the pressure and temperature profiles against altitude through the atmosphere. The first layer is the troposphere, which extends to roughly 10 km and is characterised by positive lapse rate (or decreasing temperature with altitude). At the top of the troposphere (the tropopause) the temperature stops decreasing, and then the stratosphere is defined by a negative lapse rate. This is due to UV radiation being absorbed by ozone, and leads to a very vertically stable environment.

In addition to these atmospheric layers, the troposphere can be subset into the *boundary layer* and the *free troposphere*. The *boundary layer* is the lowest layer and involves increased atmospheric mixing due to ground heating and friction effects. It generally extends anywhere from 200 - 1000 m, above which the ground effects have

fewer direct impacts. The *free troposphere* is the remainder of the troposphere and is more affected by transport, both horizontally and from the stratosphere.

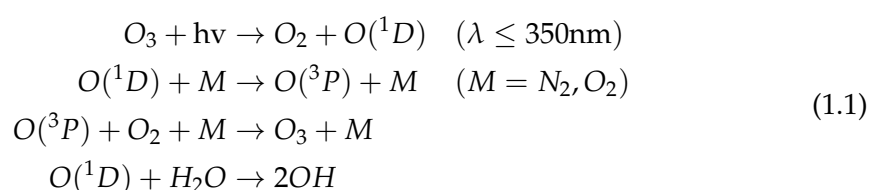
1.1.2 Composition and chemistry

There are a myriad of trace gases in the atmosphere, emitted by plants, animals, earth, and water. These gases react with one another and over time they either deposit back onto the earth or form more stable compounds such as CO₂. Oxidation and photolysis (the process of being broken apart by photons) are the two main processes whereby compounds are broken down in the atmosphere.

OH and HO₂ concentrations largely determine the oxidative capacity of the atmosphere. Concentration of the OH radical drives many processes in the atmosphere, especially during the day when photolysis of ozone produces OH (Atkinson 2000). OH is a key species which reacts with nearly all the organic compounds in the troposphere, with only a few exceptions (Atkinson 2000). Over land, isoprene (C₅H₈) and monoterpenes (C₁₀H₁₆) account for 50% and 30% of the OH reactivity respectively (Fuentes et al. 2000).

Since radicals are involved in all oxidative chemistry in the atmosphere it is important for models to accurately represent them (eg. Travis2014). This is difficult as they are coupled with so many other species and measurements of OH are not readily available on a global scale. In the late 90's it was thought that OH radicals were formed exclusively from photolysis of O₃, HONO, HCHO, and other carbonyls (R₂C=O) (Atkinson 2000). It has been shown since that OH is recycled in various processes. Isoprene (C₅H₈) was thought to be a sink of OH until it was shown by Paulot et al. (2009b) that the radicals are recycled. This recycling process is discussed in more detail in section 1.3.3.

Ozone is an important precursor to OH, as excited oxygen atoms (O(¹D)) are created through its photolysis, which then go on to react with water to form OH, as shown in this reaction sequence (Atkinson 2000; Atkinson and Arey 2003):



Where $h\nu$ represents radiation and M is an inert molecule. This shows that some of the O(¹D) recycles back to ozone, while some forms OH.

1.1.3 Radiative Forcing

One of the larger uncertainties in atmospheric modelling is how particles in the atmosphere affect radiative forcing. For 12 years it has been understood that aerosols overall cool the atmosphere, with smaller particles having a larger effect as they matching the wavelengths of visible light (Kanakidou et al. 2005). Aerosol products from gas phase emissions (or the children thereof) play an indirect and complex role in cloud properties, with a net cooling effect (Kanakidou et al. (2005), Stocker et al. (IPCC, 2013:

Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, Chapter 7,8)).

Transport and indirect effects complicate matters further, with cloud creation and modification of cloud properties being quite difficult to accurately predict. In the third IPCC report (*Intergovernmental Panel on Climate Change (IPCC): Climate Change: The Scientific Basis 2001*), the uncertainty involved if OA forcing was a factor of 3 times the estimated effect. This has since been improved however OA and cloud formation still remains a large uncertainty in more recent IPCC reports (Forster et al. 2007). Figure 1.2 shows the radiative forcing (RF) of various atmospheric constituents, it is clear that OA uncertainty dominates. Figure 1.3 shows the same summary updated in chapter 8 of the fifth report, where the SOA uncertainty remains quite large.

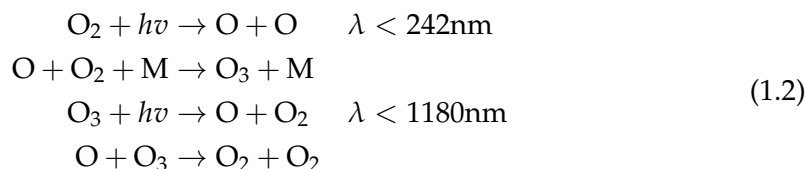
In order to improve understanding of processes involved in radiative forcing, Kanakidou et al. (2005) highlight the need for improving VOC emissions and flux measurements. They also advocate utilising satellite data in models as a means of improving the emissions inventories. VOCs can lead to changes in cloud formation, as nucleation can arise from the subsequent SOA. Kanakidou et al. (2005) concluded that it is very likely that organics contribute to particle growth and formation rates.

1.2 Ozone

Ozone (O₃) is an important greenhouse gas and oxidant. It is mostly located in the stratosphere and prevents much of the shorter wavelength (UV) solar radiation from reaching the earth's surface. Ozone in the troposphere is less beneficial, leading to health issues, radiative forcing (Stevenson et al. 2013), and crop death. Understanding and accurately portraying ozone concentrations in the troposphere is important to allow accurate predictions of future climate. This will become even more important as projections of future climate changes suggest altered vertical mixing rates, ultra violet index (UVI) and ozone RF (Hegglin and Shepherd 2009).

1.2.1 Stratospheric ozone

In the stratosphere ozone production is driven by the Chapman mechanism, as high energy radiation (with wavelengths $\lambda < 242$ nm) photolyses the molecular oxygen (O₂) in the atmosphere (Brasseur and Jacob 2017, Chapter 3, section 2). The Chapman mechanism involves several reactions which lead to rough equilibrium of O, O₂, O₃ and pressure, as follows:



The high energy photons ($\lambda < 242$ nm) are present from the top of the atmosphere but are mostly removed before reaching the troposphere as their energy is used to split the O₂ molecules. The lifetime of O against loss by O₂ is less than a second in the troposphere, and produced O₃ quickly returns to O and O₂, as low energy ($\lambda < 1180$ nm)

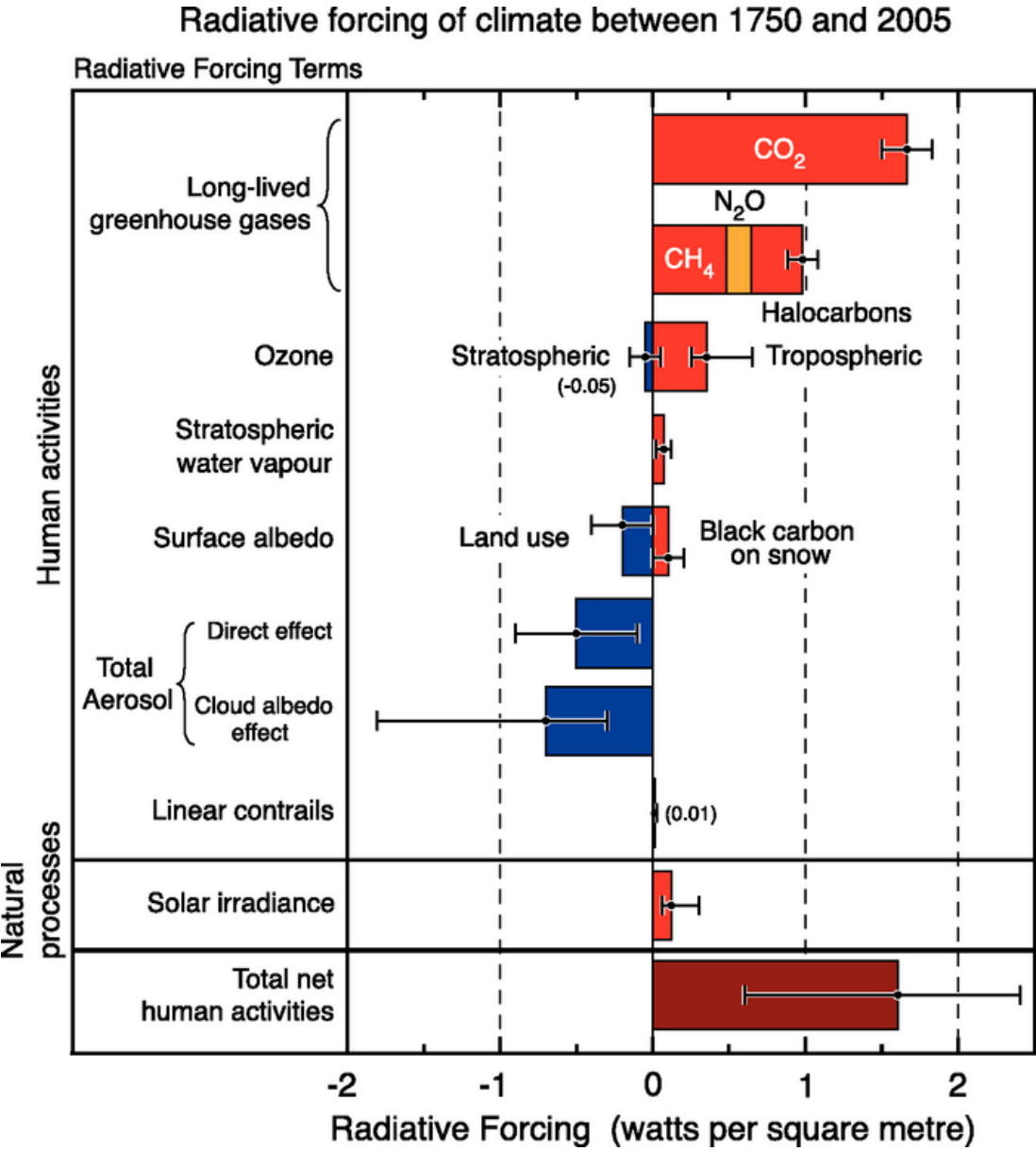


FIGURE 1.2: The overall radiative forcings and uncertainties of several atmospheric constituents This is an image taken from Forster et al. (2007), found at https://www.ipcc.ch/publications_and_data/ar4/wg1/en/faq-2-1.html.

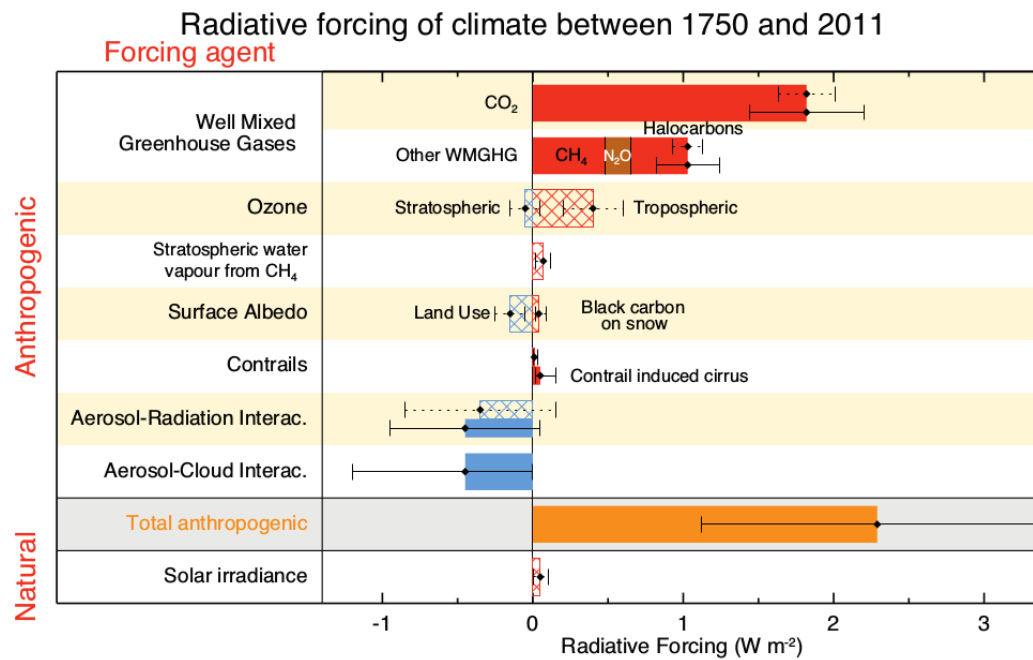


FIGURE 1.3: The overall radiative forcings and uncertainties of several atmospheric constituents. This is an image taken from Stocker et al. (IPCC, 2013: *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*), chapter 8.

photons and M are abundant. The reduced light penetration towards the surface, in addition to the logarithmic increase in atmospheric pressure (which affects M abundance) drives the vertical profile of ozone into what is called the *ozone layer*. This is a layer of relative ozone abundance within the stratosphere. The Chapman mechanism requires radiation so only takes place during the daytime, during the night this process slows to a halt, and the ozone concentrations remain stable unless pollution intrudes (Jacob 1999, Chapter 10).

Since the Montreal Protocol on Substances that Deplete the Ozone Layer was established in August 1987, and ratified in August 1989, several satellites and many measurement stations were set up to monitor ozone in the stratosphere. However, in the southern hemisphere there are relatively few records of ozone (Huang et al. 2017). This affects our ability to accurately determine sources of ozone in the troposphere.

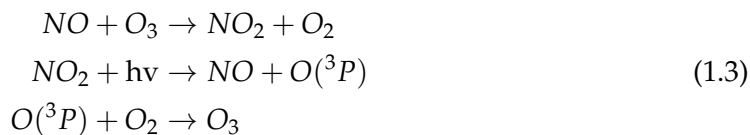
1.2.2 Tropospheric ozone

Figure 1.4, copied from Young et al. (2017), shows summary of the major processes and emissions affecting tropospheric ozone. This thesis involves improving the highly uncertain natural emissions of volatile organic compounds (VOCs) from Australia, and estimating impacts from STEs.

Generally there are two main drivers of tropospheric ozone concentrations; transport from the stratosphere and chemical production due to emissions of precursors. Tropospheric ozone is regulated by NO and NO₂ concentrations, which form an equilibrium (Cape 2008; Young et al. 2017). At small to medium scales, pyrogenic (fire) and anthropogenic (man-made) emissions can be important. Smoke plumes from biomass burning can carry ozone precursors, creating higher ozone concentrations downwind of the plume's source. Emissions of precursors from large cities (primarily traffic and power production) can impact ozone concentrations. These impacts are not always straightforward due to the nonlinear relationship between ozone and its precursors.

NO_x (\equiv NO₂ + NO) is another important chemical family in the atmosphere which interacts with ozone and regulates the atmospheric oxidative capacity. NO_x or VOC emissions affect the tropospheric ozone equilibrium and can lead to enhanced ozone formation, shown in figure 1.4. NO_x compounds are short lived, with emissions (Power generation and combustion transport) being the main driver of concentrations (Delmas, Serca, and Jambert 1997). NO_x is removed primarily by conversion to nitric acid (HNO₃) followed by wet or dry deposition (Ayers and Simpson 2006).

NO_x and O₃ relative concentrations during the day are regulated by the following reactions (Sillman 1999; Atkinson 2000):



This process with and without the influence of VOCs (panel A and B respectively) is summarised in figure 1.5.

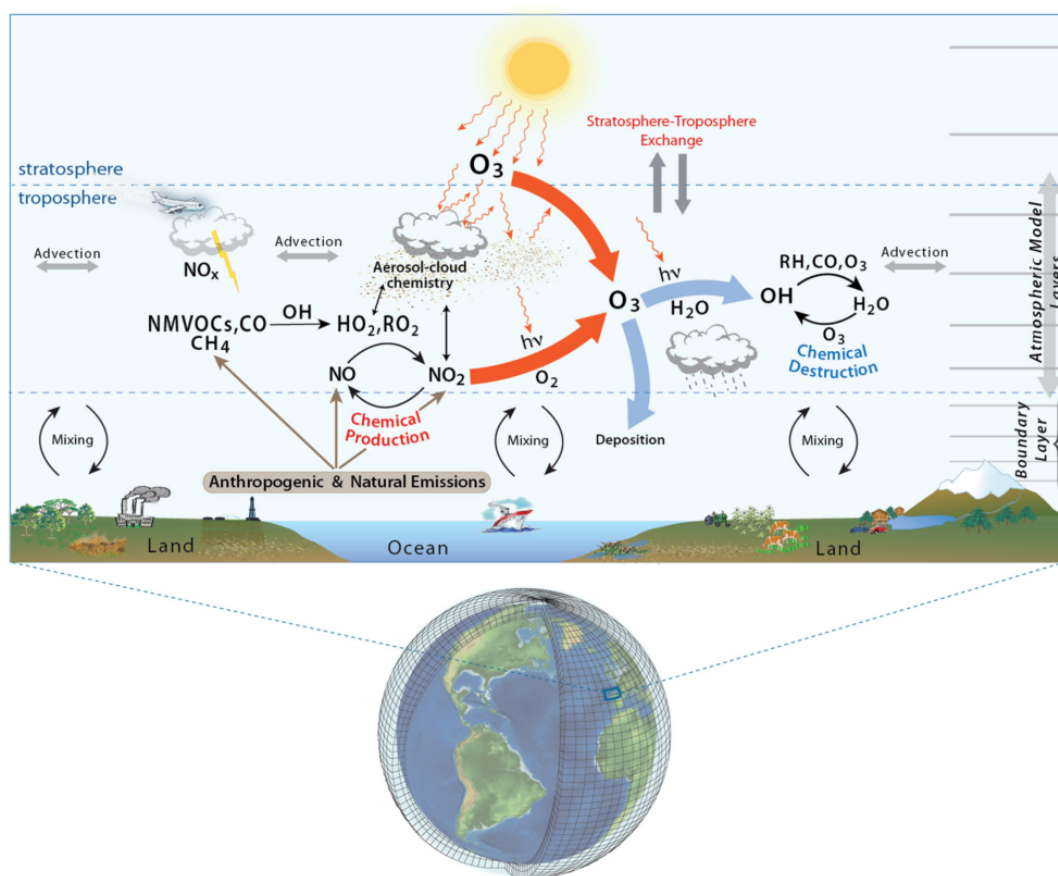


FIGURE 1.4: Tropospheric ozone processes, Figure 1 in Young et al. (2017). DOI: <https://doi.org/10.1525/elementa.265.f1>

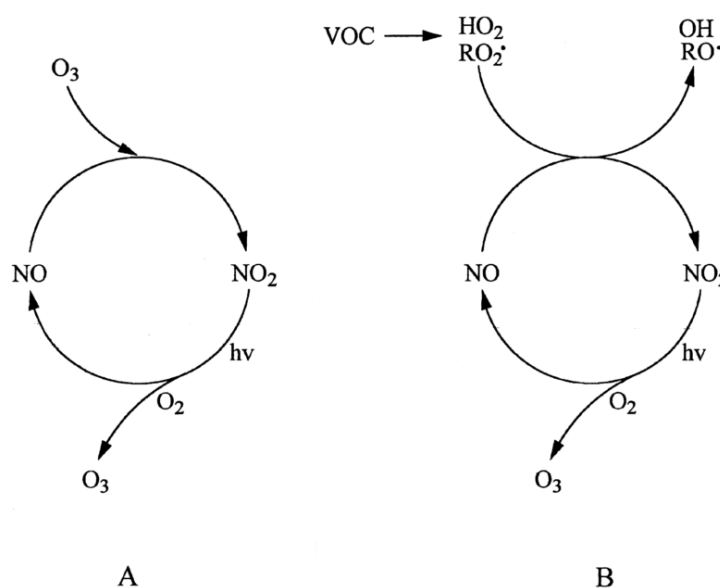


FIGURE 1.5: Figure showing NO, NO₂, and Ozone photoequilibrium cycle with and without (B, A respectively) influence from VOCs. Figure copied from Atkinson (2000).

1.2.3 Stratosphere to troposphere transport

Historically, ozone transported down from the stratosphere was thought to contribute 10-40 ppb to tropospheric ozone levels, matching tropospheric production (Atkinson 2000; Stohl et al. 2003). The proportion of tropospheric ozone due to transport from the stratosphere was revised down to around 10% over the years as measurement and modelling campaigns improved our understanding of global scale transport, mixing, and chemistry (Guenther et al. 2006; Monks et al. 2015). Intrusions of stratospheric air into the troposphere are often called Stratosphere to Troposphere Transport (STT) events. Although most tropospheric ozone comes from production, STT enhancements of ozone are measurable and can be regionally important (eg. Jacobson and Hansson 2000; Lelieveld et al. 2009; Kuang et al. 2017), and upper tropospheric ozone can be transported long distances (Cooper et al. 2004). An analysis of the Atmospheric Chemistry and Climate Model Inter-comparison Project (ACCMIP) simulations by Young et al. (2013) found STT is responsible for $540 \pm 140 \text{ Tg yr}^{-1}$, equivalent to $\sim 11\%$ of the tropospheric ozone column (Monks et al. 2015).

Ozone transported to the troposphere from the stratosphere can occur through diffusion (relatively slowly) or direct mixing (as STT). STT often occur as tongues of stratospheric air descend and get disconnected from the stratosphere, potentially due to low pressure systems and jet streams (Sprenger, Croci Maspoli, and Wernli 2003). Recently global chemical transport models (CTMs) have been used to trace how much ozone is being transported to the troposphere in this manner. There are a few methods of doing this, such as modeling ozone formed in (and transported from) the stratosphere (Ojha et al. 2016). Model based estimates require validation against

actual measurements, such as those from ozonesondes or satellites. Hegglin and Shepherd (2009) estimate that climate change will lead to increased STT. They posit that this is due to an acceleration in the Brewer Dobson circulation; which is the global scale model of transport of air in the troposphere and stratosphere. They estimate ~ 30 , and $\sim 121 \text{ Tg yr}^{-1}$ increases by 2095 (relative to 1965) in the southern and northern hemispheres respectively, up by 23% globally.

Liu et al. (2017) examine southern hemispheric ozone and the processes which control its inter-annual variability (IAV). IAV is the standard deviation of ozone anomalies from the monthly mean. They show that ozone transported from the stratosphere plays a major role in the upper troposphere, especially over the southern Indian ocean during austral winter. STT mostly impacts the upper troposphere, although some areas are impacted right down to the surface. Kuang et al. (2017) found a measurable impact of STT ozone enhancement in the south east US using several different instruments. They also show how ozone depends on both the local topography, weather systems, and trace gases emitted and transported into the region. Liu et al. (2017) examined modelled tropospheric ozone sensitivity to various meteorological parameters. They found tropospheric ozone sensitivity to emissions from South America ($0\text{--}20^\circ\text{S}$, $72.5\text{--}37.5^\circ\text{W}$), southern Africa ($5\text{--}10^\circ\text{S}$, $12\text{--}38^\circ\text{E}$), and South to South east Asia ($70\text{--}125^\circ\text{E}$, $10^\circ\text{S}\text{--}40^\circ\text{N}$). In the US recent work by Lin et al. (2015) suggests that intrusions during spring are increasing surface ozone levels. They recommend improvements to understanding of the frequency and cause of STT are needed effectively implement air quality standards.

1.2.4 Chemical production

Ozone produced in the troposphere from precursors and radiation drive ozone levels, especially in the lower (near-surface) troposphere. The main processes involved are shown in figure 1.4, with ozone regulated by reactions 1.3. As discussed above STTs source $\sim 11\%$ of the tropospheric column of ozone, with the remainder produced photochemically (Monks et al. 2015). A recent summary by Young et al. (2017) estimates ozone production and loss in the troposphere to be $\sim 4900 \text{ Tg yr}^{-1}$, and $\sim 4500 \text{ Tg yr}^{-1}$ respectively. These numbers are at the global scale, and it should be noted that meteorology and topography can play massive roles due to large spatial variability in ozone (eg. Kuang et al. 2017).

Tropospheric ozone concentrations require climate and ozone precursor emissions; including NO , NO_2 , CO , and VOCs such as HCHO (Atkinson 2000; Young et al. 2013; Marvin et al. 2017). Ozone predictions are uncertain and changing climate affects transport, deposition, destruction, and plant based precursor emissions. All of these processes are tightly coupled and difficult to accurately model, as they depend on uncertain assumptions such as CO_2 dependency (Young et al. 2013). Even with all the work done over the prior decades there remain large uncertainties about ozone precursors in the troposphere (Mazzuca et al. 2016).

Ozone is formed in the troposphere through oxidation of VOCs (described in Section 1.3) in the presence of NO_x . Net formation or loss of O_3 is determined by interactions between VOCs, NO_x , and HO_x , and is a complicated system of positive and negative feedbacks (Atkinson 2000). Figure 1.6 shows an example of this non-linear relationship between NO_x , VOCs, and ozone production as modelled in Mazzuca et al.

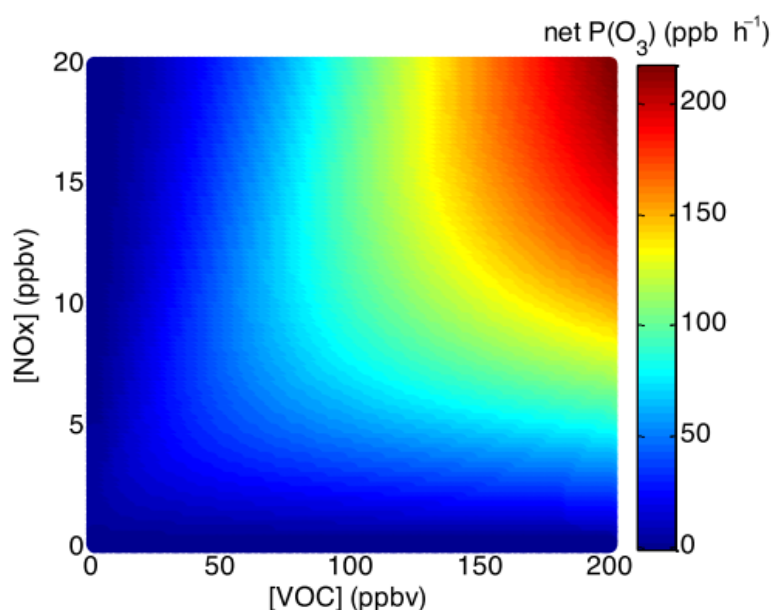


FIGURE 1.6: Ozone production rate dependent on NO_x and VOC concentrations (Mazzuca et al. 2016).

(2016). This non-linear relationship is examined in more detail in the following section (1.3). Recently the relationship has been examined on the intradiel timescale showing that ozone production can be more or less sensitive to VOCs at different hours (Mazzuca et al. 2016). This shows how important it is to correctly determine the precursors concentrations in order to estimate ozone levels and production.

Tropospheric ozone is lost via chemical destruction and dry deposition, estimated to be $4700 \pm 700 \text{ Tg yr}^{-1}$ and $1000 \pm 200 \text{ Tg yr}^{-1}$, respectively (Stevenson et al. 2006; Young et al. 2017). The main loss channel is through equation 1.1, where photolysis and collisions (increasing with pressure) create OH from the O_3 .

1.3 Volatile Organic Compounds

The least well understood precursors to tropospheric ozone production belong to a class of organic compounds. Organic compounds are members of a large class of chemicals whose molecules contain carbon, with the exception of a few compounds such as carbides, carbonates, and simple oxides of carbon and cyanide. Organic compounds can be categorised based on their vapour pressure, which is the tendency of a liquid or solid to vaporise. Compounds with high vapour pressures at standard temperature are classed as volatile, and have a tendency to evaporate at low temperatures. Plants contain tens of thousands of organic compounds, with fewer than 40 having high enough volatility to be emitted (Guenther et al. 2000). Gas phase emissions with higher vapour pressures can be oxidised into lower vapour pressure products which will partition between gas and particle phase, often called semi or non-volatile.

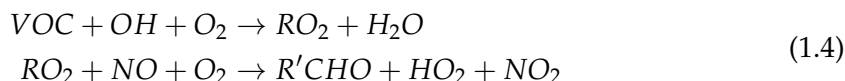
Atmospheric organic compounds are legion and differ by orders of magnitude with respect to their fundamental properties, such as volatility, reactivity, and cloud

droplet formation propensity, etc. Volatile organic compounds (VOCs) have vapour pressure greater than 10^{-5} atm, and are mostly generated naturally by plants, which emit around 1000 Tg yr^{-1} (Guenther et al. 1995; Glasius and Goldstein 2016). Due to their high volatility these compounds generally exist in the gas phase. Organic compounds with a lower volatility are classed as semi-volatile (SVOCs: vapour pressure between 10^{-5} and 10^{-11} atm) are found in both gas and particle phase depending on temperature and pressure. Organic compounds with even lower vapour pressure are generally found in the particle phase in aerosol particulate matter (Glasius and Goldstein 2016). Understanding the drivers of trends in biogenic VOC emissions (BVOCs) is required in order to estimate future carbon fluxes, changes in the water cycle, ozone production, air quality, and other climate responses (Yue, Unger, and Zheng 2015). In the last 20 years anthropogenic emissions of VOCs have been increasing while biogenic VOC emissions have decreased, due to rapid economic growth and lower annual temperatures (Stavrakou et al. 2014; Kwon et al. 2017).

Methane (CH_4) is one of the more abundant VOCs, however it is often classified separately and compared against non-methane VOCs (NMVOCs). NMVOCs include alkanes, alkenes, and aromatic hydrocarbons, with isoprene (an alkene) being the most abundant (Guenther et al. 1995). Methane is relatively long lived (years) and is well mixed in the atmosphere while other VOC levels are spatially diverse due to their shorter lifetimes. In this thesis I work towards a better understanding of the isoprene emissions coming from Australia.

VOCs are an important driver of atmospheric processes, especially near forests. VOCs are broken down into HCHO , O_3 , CO_2 and many other species, mainly through oxidation by OH . VOC emissions result in radical cycling, acid deposition, production of tropospheric ozone, and secondary organic aerosols (SOAs) (Atkinson 2000; Kanakidou et al. 2005). VOC emissions affect surface pollution levels, potentially enhancing particulate matter (PM) and ozone levels. A regional-model study in Europe (Aksoyoglu et al. 2017) has also shown VOCs impact secondary inorganic aerosol concentrations. These have impacts on climate (through radiative forcing) and air quality (from ozone and SOA enhancements), affecting both human health and crop yields (Forster et al. 2007; Avnery et al. 2013; Lelieveld et al. 2015).

Ozone in rural areas is often higher than in populous cities, due to titration of ozone by NO in polluted areas (Cooper, Gilge, and Shindell 2014; Monks et al. 2015). In areas with high VOC concentrations, ozone production may be enhanced through the following reaction sequence (Sillman 1999):



with R and R' representing organic species. The reactions of VOCs or CO with OH convert NO to NO_2 , which leads to ozone formation as NO_2 production in reaction 1 of 1.3 is bypassed.

One aspect associated with VOC emissions is the production of aerosols. Aerosols are suspended particulates and liquid compounds in the atmosphere, often called particulate matter (PM). PM in the atmosphere is a major problem, causing an estimated 2-3 million deaths annually (Hoek et al. 2013; Krewski et al. 2009; Silva et al. 2013; Lelieveld et al. 2015). Fine particulate matter ($\text{PM}_{2.5}$) penetrates deep into the lungs

and is detrimental to human health. Some PM comes from small organic aerosols (OA) emitted in the particulate phase and referred to as primary OA (POA).

A substantial amount of PM is due to gaseous organic compounds transforming in the troposphere leading to what is known as secondary OA (SOA) (Kroll and Seinfeld 2008). Formation of SOA is generally due to VOC oxidation and subsequent reactions, while removal from the atmosphere is largely due to wet or dry deposition, and cloud scavenging (Kanakidou et al. 2005). It can be difficult to attribute the formation of SOA, in part due to the complex relationship between NO_x , OH, O_3 , and the uncertainty surrounding precursor emissions. Most of the tropospheric SOA comes from biogenic precursors, the evidence for this has grown over the last two decades (Guenther et al. 1995; Kanakidou et al. 2005; Guenther et al. 2012). Improved concentration estimates of these precursors requires a better understanding of their emissions, which is one of the foci in this thesis.

Photolysis and oxidation of many VOCs initially form alkyl radicals ($R\cdot$). VOCs are removed mainly by photolysis and oxidation, but also by wet and dry deposition, reaction with NO_3 , and ozonolysis (at night time or in polluted areas) (Atkinson and Arey 2003; Brown et al. 2009). The process of deposition only accounts for a small fraction of the VOC loss, with the possible exception of the long lived methane compound (Atkinson and Arey 2003).

1.3.1 Emissions

VOC emissions are often classified as either anthropogenic, biogenic, or pyrogenic. There are ten times the mass of NMVOCs from natural sources as there are from anthropogenic sources (Guenther et al. 2006; Kanakidou et al. 2005; Millet et al. 2006). Methane and isoprene each comprise around a third of the global total emissions of VOCs (Guenther et al. 2006). Major emitters are broadleaves (notably eucalypts), and shrubs (Guenther et al. 2006; Arneth et al. 2008; Niinemets et al. 2010; Monks et al. 2015). TODO: why do plants emit? increased canopy light penetration? Emissions are affected by various factors such as temperature, sunlight, soil moisture, etc. The ocean also plays a role in VOC emissions, with the Oceanic Niño Index (ONI) showing positive VOC emission anomalies associated with neighbouring countries (Stavrakou et al. 2014).

Globally around 710 - 1150 Tg C yr^{-1} of BVOCs are emitted (Lathière 2016; Guenther et al. 1995; Lathière et al. 2006; Guenther et al. 2012). 90% of these emissions come from plants and trees, with the most dominant species being isoprene (C_5H_8) ($\sim 50\%$), monoterpenes ($\text{C}_{10}\text{H}_{16}$), methanol (CH_3OH), ethanol ($\text{C}_2\text{H}_6\text{O}$), acetaldehyde (CH_3CHO), acetone ($(\text{CH}_3)_2\text{CO}$), ethene (C_2H_4) and propene (C_3H_6) (together making up $\sim 30\%$) (Guenther et al. 2012). Many of these estimates come from MEGAN, a bottom-up biogenic emissions model which is highly sensitive to several parameters including soil moisture and plant functional type. MEGAN has recently been analysed using 30 years of meteorological reanalysis information by Sindelarova et al. (2014). They estimate emissions of Biogenic VOCs (BVOCs) to be 760 Tg C yr^{-1} , 70% (532 Tg C yr^{-1}) of which is isoprene. This is similar to isoprene emission estimates from MEGAN itself, of 400-600 Tg C yr^{-1} (Guenther et al. 2006). Another model (ORCHIDEE, with inputs similar to MEGAN) estimates 752 ± 16 Tg C yr^{-1} , sensitive to terrestrial vegetation variations (Lathière et al. 2006). MEGAN emissions estimates are

termed bottom-up, as opposed to top-down which are derived from satellite measurements of the products of various VOCs. Using GOME satellite HCHO and a Bayesian inversion technique to derive isoprene emissions, Shim et al. (2005) estimated global isoprene emissions to be $\sim 566 \text{ Tg C yr}^{-1}$. This estimate decreases simulated OH concentrations by $\sim 10\%$, to $9.5 \times 10^5 \text{ molec cm}^{-3}$.

Global VOC levels are estimated at 85 %, 13 %, and 3 % from biogenic, anthropogenic, and pyrogenic sources respectively (Kanakidou et al. 2005; Kefauver, Filella, and Peñuelas 2014). Methane makes up a third of atmospheric VOCs and is relatively ubiquitous due to its longer lifetime. The main non-methane BVOC emissions are isoprene (44%) and monoterpenes (11%) (Guenther et al. 2000; Kefauver, Filella, and Peñuelas 2014). Land use changes can drastically affect isoprene sources, for instance in the tropics where large scale deforestation has converted forest into crop lands (Kanakidou et al. 2005). Due to the lack of in-situ ground based measurements, estimates of VOC emissions are uncertain, with large scale extrapolation required (Millet et al. 2006). In this thesis I'll be focusing on emissions of isoprene.

1.3.2 Isoprene

Isoprene, or 2-methylbuta-1,3-diene, is a VOC with the chemical formula C_5H_8 . It is of major importance to the atmosphere, as it is involved in various processes which alter the oxidative capacity of the atmosphere. Isoprene affects NO_x and HO_x cycling, see for example formulae 1.1, 1.3. In the presence of NO_x , isoprene forms tropospheric ozone and SOAs (Wagner 2002; Millet et al. 2006). It has a short lifetime during the day, roughly an hour due to OH oxidation (Atkinson and Arey 2003).

Guenther et al. (1995), and subsequent updates (Guenther et al. 2000; Guenther et al. 2006; Guenther et al. 2012), have been used ubiquitously by the atmospheric community as a global estimate of isoprene emissions, at roughly $500\text{--}600 \text{ Tg yr}^{-1}$, emitted mostly during the day. Recently an estimate of global isoprene emissions, of around 465 Tg C yr^{-1} , has been made using a completely different model (Messina et al. 2016). The global emission factors used to derive both these estimates are based on modelling emissions from different plant species (phenotypes), and relatively few Australian species are used when forming in these estimates.

Measurements of isoprene are often uncertain or difficult to make accurately. Chamber experiments are used to determine how isoprene behaves once it is emitted into the atmosphere, however reaction rates may be unsuitable to the natural atmosphere which is often very different (Kanakidou et al. 2005; Nguyen et al. 2014). Improving chamber study methods could improve understanding of ambient atmospheric oxidation mechanisms of biogenic hydrocarbons (such as isoprene), which could reduce some of the high uncertainties involved with VOC chemistry (Nguyen et al. 2014). Uncertainties in emissions however require different techniques and measurements in order to be improved.

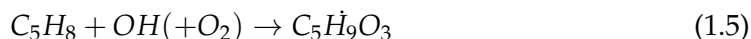
Isoprene emissions estimates are still fairly uncertain, as global measurements are difficult and regional emissions can be very different. The global uncertainty of isoprene emission was estimated to be a factor of 2 to 5 ($250\text{--}750 \text{ Tg yr}^{-1}$) (Kanakidou et al. 2005). Improvements over the years have been incremental, and generally localised to regions of particular interest for air quality such as China and the USA TODO: find recent uncertainty estimate improvements examples. The lack of accuracy in BVOC

emissions estimates prevents accurate determinations of the sources and distribution of pollutants including ozone and organic aerosols. Accuracy in VOC measurements is important: it has been shown that even the diurnal pattern of isoprene emissions has an effect on modelling ground level ozone (Hewitt et al. 2011; Fan and Zhang 2004).

1.3.3 Isoprene chemistry

Isoprene forms many products with various lifetimes, here I will present an overview of some important mechanisms and products. Isoprene is emitted and enters the atmosphere in the gas phase, where it reacts quickly with OH and other radicals. One common compound which is produced by these reactions is HCHO, which is easier to measure and often used to estimate how much isoprene is being emitted. Alkenes (VOCs with double bonded carbon, such as isoprene) react with OH, ozone, or NO₃, leading to organic peroxy radicals (ROO[•]). These go on to form many products and lead to (amongst other things) aerosol, formaldehyde, and ozone formation, depending on sunlight and NO_x concentrations (Atkinson 2000). Reactions with NO can lead to ozone production within environments rich in isoprene or other NMVOCs (PATCHEN et al. 2007; Atkinson and Arey 2003).

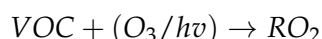
Figure 1.7 shows the first stages of oxidation of isoprene by OH. Isoprene reactions are important to understand due to their impacts on air quality, ozone, and physical properties in the lower troposphere. The primary first step for atmospheric isoprene is photooxidation, reacting with OH to form isoprene hydroxyperoxy radicals (ISOPOO - a subset of ROO[•]) (Patchen2017; Wolfe et al. 2016; Marvin et al. 2017). This is largely split into two types of ISOPOO, based on which carbon the OH adducts to (see figure 1.7).



The many children processes and products which begin with isoprene oxidation are often called the isoprene (photochemical) cascade (Paulot2012; eg. Crounse et al. 2012; Wolfe et al. 2016).

Oxidation

The primary sink for isoprene is oxidation by OH. First isoprene has its double bond replaced by OH, as summarised by the equation from PATCHEN et al. (2007): $R-CH=CH-R' + OH \rightarrow R-CH(OH)CH-R'$ where R and R' represent hydrocarbons. Ozonolysis and photolysis are lesser oxidation pathways for volatile alkenes, involving the splitting of carbon chains by ozone molecules or photons respectively:



(Nguyen et al. 2016; Wolfe et al. 2016). Ozonolysis also leads to HCHO, with yields depending on subsequent reactions.

After oxidation by OH, the adducted OH then reacts with O₂ to produce ISOPOO, which can be any of six different isomers (PATCHEN et al. 2007). ISOPOO reacts with HO₂ or NO, producing stable products (often called oxidised VOCs or OVOCs). One important product produced (with varying yields) through each oxidation pathway is

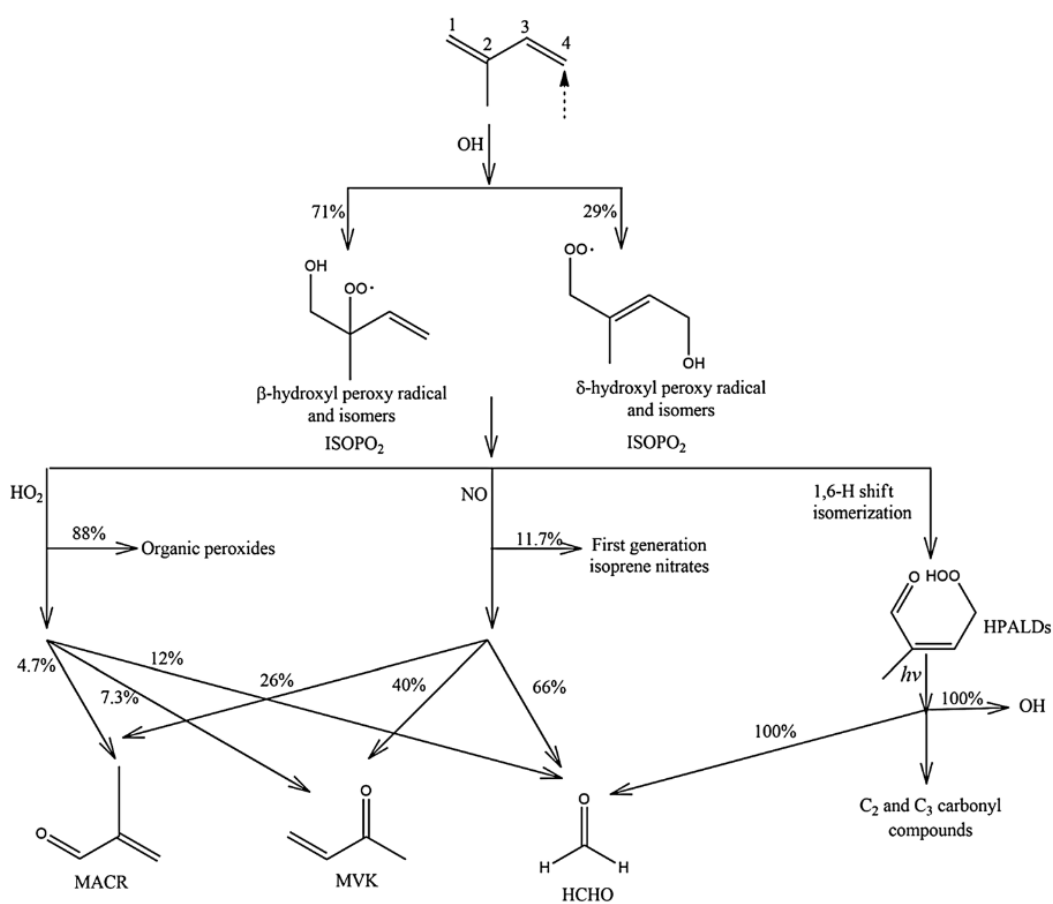
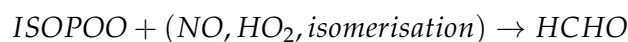


FIGURE 1.7: Isoprene products following oxidation by OH, figure from Mao et al. (2013)

HCHO:



During the day HCHO has a lifetime of 1-2 hrs, while ROO[•] lasts ~ 100 s, making reaction 1.5 a rate limiting factor in HCHO production (Wolfe et al. 2016). ISOPOO also can isomerise and produce HPALDS (see figure 1.7), which also leads to HCHO.

There is uncertainty about which pathways are most important following ISOPOO production, affecting predictions by atmospheric models (Nguyen et al. 2014). This limits understanding of the relative importance of some chemical processes, such as auto-oxidation (of ISOPOO and other ROO[•]) (Crounse et al. 2013). The reaction pathways depend on local concentrations of NO_x: the high and low NO_x pathways are dominated by NO and HO₂ reactions respectively. HO₂ reactions predominantly produce hydroxyhydroperoxides (ISOPOOH), while NO reactions produce isoprene nitrates (ISOPN) (Crounse et al. 2006). If measured, first generation ISOPN and ISOPOOH products can be used to determine the portion of isoprene oxidation following each pathway (eg. Yu et al. 2016). Globally around one third of ISOPOO react with HO₂, and two thirds react with NO (Paulot et al. 2009b). Most of these reaction pathways produce HCHO, however this along with methyl vinyl ketone (MVK), and methacrolein (MACR) are formed at different yields between the two pathways (Marais et al. 2012; Liu et al. 2016b; Wolfe et al. 2016).

High NO_x pathway

In the presence of NO_x, ISOPOO reacts with NO and forms ISOPN, which affect levels of both HO_x (H, OH, peroxy radicals) and NO_x. ISOPN generally act as a sink of HO_x, and can be a sink or reservoir for NO_x (Mao et al. 2013). A portion of the ISOPN are recycled back to NO_x, serving as a reservoir of nitrogen and allow its transport to the boundary layer of remote regions (PATCHEN et al. 2007; Paulot et al. 2009a; Yu et al. 2016). The nitrates can also build up in the winter, when removal processes are not as dominant (Lelieveld et al. 2009). Reactions of OH with NO₂ are the main radical sink in high-NO_x systems (Wolfe et al. 2012).

First generation ISOPN produce MVK($\sim 40\%$), MACR($\sim 26\%$), and HCHO($\sim 60\%$) at higher yields than is produced by ISOPOOH (Liu et al. 2013; Mao et al. 2013). The MVK and MACR products form additional HCHO within a few hours due to oxidation by OH (Palmer et al. 2006). Under high NO_x conditions there is a higher and faster yield of HCHO, with most of the ultimate HCHO production occurring within one day (Palmer et al. 2006).

Low NO_x pathway

In low NO_x environments, ISOPOOH is formed in yields $> 70\%$, while MACR, MVK, and HCHO are formed at $\sim 5\%$, $\sim 7\%$, and $\sim 12\%$ respectively (Paulot et al. 2009b; Mao et al. 2013). This ISOPOOH mostly reacts with OH to form IEPOX while regenerating OH (Mao et al. 2013). This pathway has lower and slower ultimate yields of HCHO from isoprene emissions when compared to the high-NO_x pathway (Palmer et al. 2006).

Isoprene oxidation and subsequent reactions are less well understood when lower concentrations of NO are present in the atmosphere. It was thought that in low NO

environments, like those far from anthropogenic pollution and fires, oxidation of isoprene would create ISOPOOH and reduce local concentrations of OH and HO₂ (Guenther et al. 2000; Paulot et al. 2009b). However this reduction was not seen in measurements and HO_x levels have been shown to be largely unaffected by isoprene concentrations (Paulot et al. 2009b). HO_x is recycled through dihydroxyperoxides (IEPOX), formed from ISOPOOH oxidation, and some HO_x is produced in the formation of MACR and MVK (Paulot et al. 2009b). Paulot et al. (2009b) estimated that 95 ± 45 Tg yr⁻¹ of IEPOX was being created in the atmosphere, which (at the time) was not modelled by CTMs. Peeters and Muller (2010) suggested that the work of Paulot et al. (2009b) only partially bridges the gap between clean air OH concentration measurements and models. They suggested four new mechanisms for OH recycling in these pristine conditions. These can be summarised as OH regenerating reactions which occur during photolysis of hydroperoxy-methyl-butenals (HPALDs), and resulting photolabile peroxy-acid-aldehydes (PACALDs). These reactions are highly non-linear and subject to large uncertainty, however they were shown to improve modeled HO_x concentrations against several campaigns. Peeters and Muller (2010) showed that HO₂ is produced at near unity yields following isoprene oxidation initiated by OH. Their results were backed up by observations of OH recycling observed in low NO conditions (Crounse et al. 2012).

Uncertainties and bias from measurements have made it more difficult to understand what happens in low NO_x conditions as many observations of OH were still quite under-predicted in models (Mao et al. 2012). Due to OVOC interference, measurements in low NO_x environments can lead to massively overestimated MVK and MACR yields (Nguyen et al. 2014). Nguyen et al. (2014) show preliminary estimates of low-NO yields of MVK and MACR to be $6 \pm 3\%$ and $4 \pm 2\%$ respectively, consistent with TODO:Liu et al. (2013), but only when cold-trapping methods are employed. Mao et al. (2012) showed that many instruments were generating OH internally. Model and measurement corrections have helped closed the gap between model predictions and detected concentrations of VOCs and OH (Mao et al. 2012).

Even with the recent boom in isoprene analysis, uncertainties remain in the isoprene oxidation mechanisms. Examples (taken from Nguyen et al. (2014)) include isoprene nitrate yields, which range from 4-15% (Paulot et al. 2009a), 90% disagreements in MACR and MVK yields (Liu et al. 2013), various possible sources for SOA (Chan et al. 2010; Surratt et al. 2010; Lin et al. 2013), unknown HPALD fates, incomplete O₂ incorporation (Peeters, Nguyen, and Vereecken 2009; Crounse et al. 2013), and under-characterised RO₂ lifetime impacts (Wolfe et al. 2012).

Night time processes

At night when OH concentrations have dropped, isoprene can remain in the atmosphere. Typically less than half of this night time isoprene is removed through ozonolysis (Atkinson and Arey 2003), however, in polluted areas where high levels of NO_x exist, isoprene is consumed by nitrate radicals (NO₃), which joins to one of the double bonds and produces organic nitrates in high yield (65% to 85%) (Mao et al. 2013). (todo: read mao2013 para 3 cites) NO₃ are largely formed through ozone reactions, as in equation 1.3. A build up of NO₃ radicals can be seen at night, when photolysis is not removing them (Atkinson 2000; Brown et al. 2009).

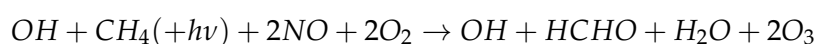
In areas with high NO_x levels, greater than 20% of the isoprene emitted late in the day ends up being oxidised by the NO_3 radical overnight (Brown et al. 2009). At night isoprene affects on both NO_x concentrations and ozone levels, and can form harmful organic nitrates and SOAs (Brown et al. 2009; Mao et al. 2013). These nitrates go on to produce further SOAs, largely due to NO_3 reacting with first generation isoprene oxidation products (Rollins et al. 2009). The night-time concentrations of OH and ozone also have a complex effect on NO_x removal in high latitude winters, when photolysis and NO reactions are reduced (Ayers and Simpson 2006).

1.4 Formaldehyde

formaldehyde (HCHO), aka methanal, methyl aldehyde, or methylene oxide, is of the aldehyde family. HCHO is an OVOC which is toxic, allergenic, and a potential carcinogen. In this thesis HCHO is used to estimate isoprene emissions over Australia. One of the major products of isoprene chemistry is HCHO. HCHO is important both for its own atmospheric impacts, and as a proxy for determination of isoprene emissions. Given a modelled yield of HCHO from isoprene, it is possible to work backwards from measured HCHO concentrations to determine the isoprene emissions. HCHO production does depend on NO_x concentrations, as it affects the yield from isoprene oxidation. HCHO yield is higher in the high- NO_x pathway (compared to the low- NO_x pathway) from isoprene reactions (Marais et al. 2012).

1.4.1 Sources and sinks

Background levels of HCHO in the atmosphere are driven by the oxidation of methane (CH_4) by the hydroxyl radical (OH), which produces $\sim 970 \text{ Tg yr}^{-1}$ (Fortems-Cheiney et al. 2012). Atkinson (2000) summarised the background formation of HCHO with the following reaction:



which shows that photolysis and oxidation of methane forms HCHO and ozone in a process that regenerates the OH radicals. CH_4 concentrations are relatively well constrained in models, with the ACCMIP comparison showing only $\sim 3\%$ inter-quartile range (Young et al. 2013). There is a complex relationship between VOCs, HO_x , and NO_x : with higher levels of NO_x increasing the rate at which VOCs are converted into HCHO (Wolfe et al. 2016).

Within the continental boundary layer (CBL), HCHO is enhanced above background HCHO levels, due to NMVOC emissions reacting with OH radicals in the presence of NO_x (Wagner 2002; Millet et al. 2006; Kefauver, Filella, and Peñuelas 2014). The total contribution from NMVOC oxidation is $\sim 358 \text{ Tg yr}^{-1}$ (Fortems-Cheiney et al. 2012). Enhancements to regional and continental HCHO are largely driven by isoprene emissions (Guenther et al. 1995; Palmer 2003; Shim et al. 2005; Kefauver, Filella, and Peñuelas 2014). This is true except near fires or anthropogenic sources of HCHO and precursors (Guenther et al. 1995; Kefauver, Filella, and Peñuelas 2014; Wolfe et al. 2016). Biomass burning (BB) can be a source of HCHO, and various

other pollutants, precursors, and aerosols (Guenther et al. 1995; Andreae 2001). Additionally HCHO is emitted into the atmosphere directly through fossil fuel combustion, natural gas flaring, ethanol refining, and agricultural activity (Wolfe et al. 2016).

Other terpenoids (monoterpenes, sesquiterpenes, etc.) can also produce HCHO, although generally to a lesser extent than isoprene, methane and biomass burning (Guenther et al. 2012). Many of the HCHO yields from terpenoids are estimated through chamber studies which examine molecular mass and charge after mixing the compound of choice into a known volume of air (eg. Nguyen et al. 2014). These conditions generally don't match those of the real world, where ambient air will have a cocktail of these compounds and other reactants. One issue with chamber studies is the difficulty they have trying to accurately reproduce ambient outside air, which limits the scope to which the studies may be applied (Nguyen et al. 2014).

Anthropogenic sources of HCHO are largely negligible, however in very large cities or by using oversampling techniques an anthropogenic signal can be found (Millet et al. 2008; Zhu et al. 2014). If the population centres and industrial districts are large enough they can emit huge amounts of VOCs into the atmosphere (Fu et al. 2007), leading to increased surface ozone levels (Zhu et al. 2014) In Australia this is not yet a major issue, however anthropogenic sources of pollution can be detected (see section 2.6.2).

In the past, HCHO levels were underestimated by models, often with large discrepancies, due to the poor understanding of methyl peroxy radical (CH_3OO) chemistry (Wagner 2002). Nowadays HCHO concentrations are better understood, however precursor emissions are one of the main unknowns (eg. Emmerson et al. 2016; Marvin et al. 2017). Marvin et al. (2017) found that discrepancies in modelled HCHO concentrations are primarily due to second and later generation isoprene oxidation chemistry.

HCHO has two major sinks, reactions with OH (oxidation), and photolysis (adding up to $\sim 1210 \text{ Tg yr}^{-1}$) (Levy 1972; CRUTZEN, LAWRENCE, and PÖSCHL 1999; Wagner 2002; Fortems-Cheiney et al. 2012; Kefauver, Filella, and Peñuelas 2014). These reactions lead to a daytime lifetime of a few hours (Atkinson 2000; Millet et al. 2006). Both these loss processes (photolysis, oxidation) form CO and hydroperoxyl radicals (HO_2), and have global significance to radiative forcing and oxidative capacity (Franco et al. 2015). The other major sinks are wet and dry deposition, although these are not as significant ($\sim 32 \text{ Tg yr}^{-1}$) (Atkinson 2000; Fortems-Cheiney et al. 2012).

1.4.2 Measurement techniques

There are a few ways to measure HCHO, including Fourier Transform Infra-Red (FTIR) Spectrometry and Differential Optical Absorption Spectroscopy (DOAS). FTIR examines the Fourier transform of a measured spectrum in order to detect things which affect that spectrum. DOAS methods are based on light interference and absorption through air masses.

The DOAS technique takes advantage of the optically thin nature of HCHO in order to linearise the radiance differential through air masses with and without HCHO, using the Beer-Lambert intensity law. This method is used both on the ground, and from space, globally for HCHO detection (Guenther et al. 1995; Gonzalez Abad et al. 2015; Davenport et al. 2015). As a trace gas HCHO interferes with light over a

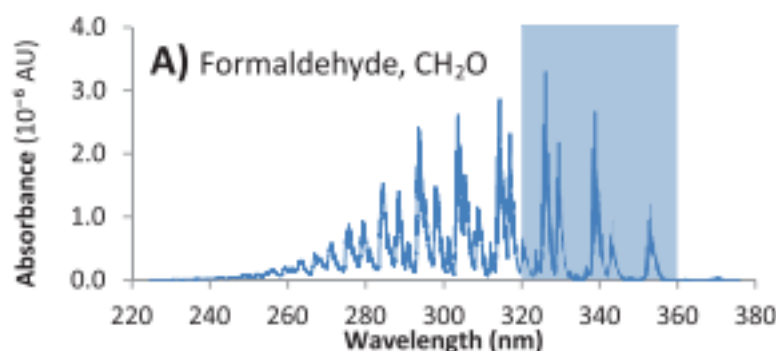


FIGURE 1.8: HCHO spectrum, with a typical band of wavelengths used for DOAS path measurements. This is a portion of an image from Davenport et al. (2015).

few wavelength bands, which allows instruments to detect concentrations between a known light source and a detector. Figure 1.8 shows the interference spectrum of HCHO along with a typical band used to examine interference in the DOAS technique. One difficulty is that this interference is relatively small (HCHO is optically thin) and other compounds absorb light at similar wavelengths (Davenport et al. 2015).

FTIR and DOAS measurements have a range of uncertainties, including systematic and random measurement errors and uncertain apriori shape factors and water profiles (eg: Franco et al. (2015)). Other types of measurement involve directly measuring the air, and determining chemical compounds through their physical properties such as by mass spectrometry analysis of mass to charge ratios (m/z) of ionised air masses. Two examples of this include proton transfer reaction mass spectrometers (PTR-MS), and gas chromatography mass spectrometers (GC-MS). These instruments can be used to determine gas phase evolution of isoprene and monoterpene products such as HCHO (eg. Lee et al. 2006a; Nguyen et al. 2014; Wolfe et al. 2016; Lerner et al. 2017).

Other measurement techniques include chromatographic and fluorimetric methods, both of which differ widely from each other and the spectroscopic methods (Hak et al. 2005). Hak et al. (2005) examine a single air mass with 8 instruments using the four techniques (MAX-DOAS, FTIR, chromatographic, and fluorimetric), and show that reasonable agreements can be achieved. Generally the measurements were close, the five Hantzsch instruments agreeing to within 11% (after removing two potentially faulty measurements), although different calibration standards were used. Titration for the different calibration solutions could not be resolved, which may account for absolute offsets up to 30%. These differences and non-uniformities between measurements (even among identical instruments) are part of the reason HCHO does not have a consistent network for global measurements like those for greenhouse gases or ozone (Fortems-Cheiney et al. 2012).

Satellite measurements

Satellites remotely sense atmospheric HCHO through irradiance measurements of solar light which has reflected off the earth's surface. These irradiances are affected by

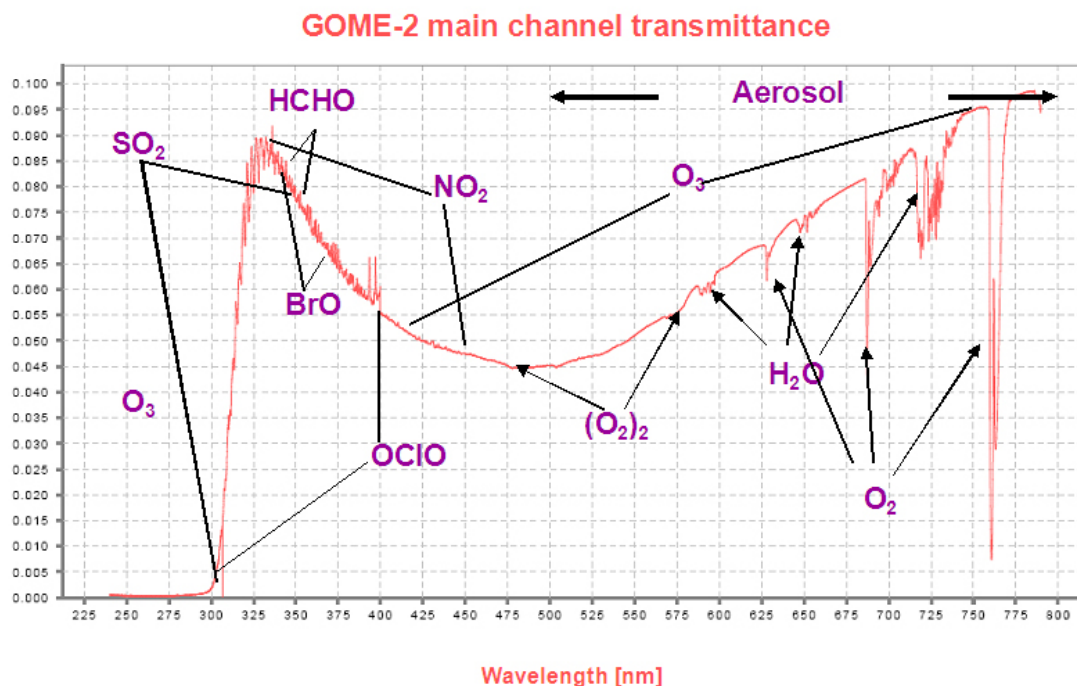


FIGURE 1.9: An example spectrum showing interferences used for species concentration measurements by GOME-2. Image by EUMETSAT and ESA (EUMETSAT 2015).

gases which exist along the reflected path of light between the detector, earth, and sun. The irradiance is then used to estimate how much of a particular gas exists along this path, which gives us an estimate which is called a slant column (SC). The retrieved SC of a particular gas (or species) can be transformed into a vertical column (VC) by scaling the path length in conjunction with accounting for the trace gas' light scattering properties. The scaling coefficient created to transform from SC to VC is called the Air Mass Factor (AMF).

Several satellites provide long term trace gas observations with near complete global coverage, including the ERS-2 launched in April 1995 which houses the GOME ultraviolet and visible (UV-Vis) spectrometer, the AURA launched in July 2004 which houses the OMI UV-Vis spectrometer, the MetOp-A and B launched in October 2006 and September 2012 respectively both housing a GOME-2 UV-Vis spectrometer. These satellites are on Low Earth Orbit (LEO) trajectories and overpass any area up to once per day. Satellites use DOAS techniques with radiative transfer calculations on solar radiation absorption spectra to measure column HCHO. An example of a spectrum retrieved from the GOME-2 instrument is given in figure 1.9.

In conjunction with atmospheric chemistry and radiative models, satellite measurements quantify the abundance of HCHO in the atmosphere. Isoprene is hard to measure directly due to its short lifetime and weak spectral absorption, instead HCHO is often used as a proxy (Millet et al. 2006; Fu et al. 2007; Dufour et al. 2008; Marais et al. 2012; Bauwens et al. 2013; Kefauver, Filella, and Peñuelas 2014; Bauwens et al. 2016; Surl, Palmer, and González Abad 2018). This leads to a method of isoprene

emissions estimation termed top-down (as opposed to bottom-up estimates). The existence of satellite data covering remote areas provides an opportunity to improve VOC emissions estimates leading to more robust models of global climate and chemistry. Satellite data gives us another way to estimate large scale isoprene emissions, and their subsequent chemistry. This method is described in detail in section 3.2.

1.5 Atmospheric Chemistry Modelling

Models can fill the gaps (both spatial and temporal) in measurement records, and can help us improve our understanding of the natural world. They are used to examine future outcomes resulting from changing our emissions, from small to large scales. They can be used to increase measurement accuracy (for instance in satellite measurements) and determine where we lack information, while also checking the performance of new instruments. Precisely representing various chemicals and reactions in the atmosphere allows efficient mitigation of pollution, since we can compare scenarios against one another. Models can always be expanded to include new compounds or processes, however validation is always necessary. Currently they require improved isoprene emissions and subsequent chemistry understanding for effective air quality determination (Marvin et al. 2017).

1.5.1 Box models

Box models are much smaller scale than global CTMs, examining one uniform environment with many parametrisations such as transport and emissions. Box models can be used to check chemical mechanisms in specific scenarios, such as high or low NO_x environments. For example: Marvin et al. (2017) use a box model matching conditions in southeast USA to evaluate isoprene mechanisms from several models. A box model involves modelling chemistry in a singular set of conditions without transport or any spatial gradients.

By allowing for interactions between boxes this concept can be extended to multiple box models. These are simply multiple instances of single boxes with the addition of transport between them, which requires meteorological fields such as wind velocities and turbulence. The meteorology fields can be modelled, and/or input as parameters.

1.5.2 Chemical transport models

Chemical transport models (CTMs) provide a simulation of chemical densities and transport over time, through the atmosphere. They require many inputs (such as wind velocities) in order to accurately represent scenarios or regions on earth. Models of emissions are often used as drivers for atmospheric chemistry models, which require initial and boundary conditions in order to run. Chemistry in the atmosphere is a complex system of coupled reactions and dynamics, which can be solved using numerical partial differential equation solvers.

CTMs simulate production, loss, and transport of chemical species. This is generally calculated using one or both of the Eulerian (box) or Lagrangian (puff) frames of reference. CTMs normally solve continuity equations simultaneously for many coupled species. The continuity equations describe transport of a conserved quantity such

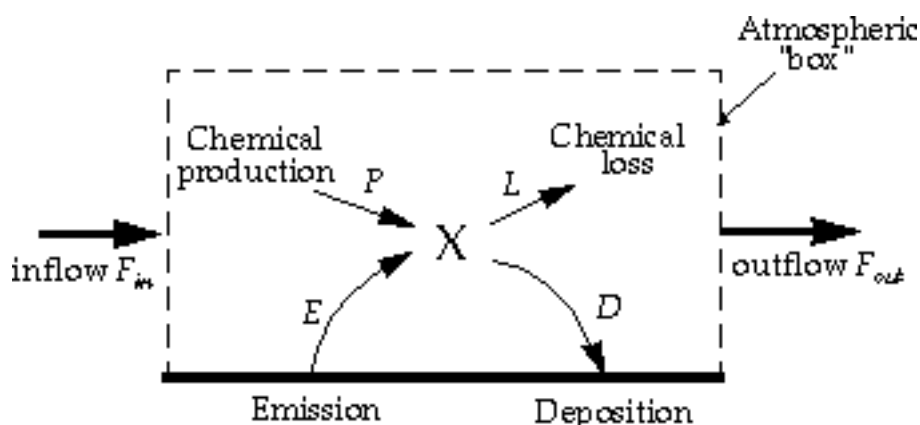


FIGURE 1.10: Standard box model parameters, image taken from Jacob (1999).

as mass or energy, which, solved together with production and loss of a chemical can provide detailed simulations of natural processes.

The general continuity equation links a quantity of a substance (q) to the field in which it flows and can be described by the formula:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot j = \sigma$$

where ρ is density of q in the field, t is time, ∇ is divergence, j is the flux (q per unit area per unit time entering or leaving the field), and σ is the generation or loss of q per unit volume per unit time.

The type of model best suited to modelling the entire earth uses the Eulerian frame of reference, where the atmosphere is broken up into 3-D boxes with densities and transport calculated and stored for sequential steps in time at each location. The mass balance equation must be satisfied in any realistic long term model and is as follows:

$$\begin{aligned} \frac{dm}{dt} &= \sum \text{sources} - \sum \text{sinks} \\ &= F_{in} + E + P - F_{out} - L - D \end{aligned}$$

where m is mass of a chemical, E and D are emission and deposition, P and L are production and loss, and F is chemical transport in and out, as shown in figure 1.10. Many chemical species interact with each other through production and loss. Any large chemical model will solve this mass balance equation over highly coupled arrays of partial differential equations, which becomes computation time expensive as complexity increases.

Contemporary models generally use mathematical differential solving tools of various complexity (often called chemical mechanisms) to solve chemical equations in order to predict chemical species evolutions over time. Different solvers may be slower or faster and more suited to particular situations based on the stability of the equations and systems involved, and chemical mechanisms may vary in how many reactions and chemicals are listed and grouped together. For example: Since $[O] \ll [O_3]$ the

chemical family O_X ($O_X \equiv O + O_3$) can be used to simplify chemistry simulations and approximate O_3 concentrations (Brasseur and Jacob 2017, Chapter 3). Different chemical mechanisms may find different solutions to the same problems, due to how the numerical solvers are implemented, which can affect model output (Zhang et al. 2012).

1.5.3 Emissions

There are two commonly used ways of estimating isoprene emissions, top-down or bottom-up. Bottom-up emission estimates generally model the flora which emit isoprene, along with the rates of emissions and things which affect these rates. Isoprene is emitted by trees or shrubs, depending on several parameters such as leaf area index (LAI), emission factors (EF), plant functional type (PFT), and light density fraction (LDF). Models use these properties of the emitters in order to estimate how much isoprene is being produced (eg. Guenther et al. 1995; Guenther et al. 2006). Understanding how much isoprene is emitted, when and by what, is complicated. One frequently used bottom up emissions model is the Model of Emissions of Gases and Aerosols from Nature (MEGAN, Guenther et al. (1995)). Since little data exists with which to verify many of these bottom-up emission inventories, they can be uncertain on a large scale.

Bottom up models of VOC emissions are sensitive to parameters. For example Stavrakou et al. (2014) examined modelled Asian emissions and altered model parameters for temperature, plant type emission factors, incoming solar radiation (insolation) intensity, land use changes, and palm tree forest expansion. Changes were constrained by a network of radiation measurements and some experiments with south east Asian forest emissions - and led to reduction in apriori isoprene emissions by a factor of two over the region in 2005. Sensitivity to these factors is pervasive in bottom up emissions models (eg. Marais et al. 2014; Miller et al. 2014; Messina et al. 2016). One of the important uncertainties seen in MEGAN is the isoprene emissions due to PFTs. If one plant species is emitting heavily near a measuring instrument, possible overestimations may occur due to extrapolation over the entire forest. Global emissions inventories like MEGAN often have large areas based on extrapolations which introduces uncertainties (Miller et al. 2014). Current emissions estimates require more validation against observations, and recently a comparison of two major VOC models (MEGAN and ORCHIDEE) was undertaken by Messina et al. (2016) reiterating this requirement. In their work they examine model sensitivities and show that the most important parameters are LAI, EF, PFT, and LDF. There is high uncertainty in LAI and EF, which require more or improved measurements at the global scale, as well as more PFTs and improved LDF parameterisation (Messina et al. 2016).

1.5.4 Uncertainties

Here I will attempt to list and partially explain the major uncertainties models have in relation to VOCs, and ozone. TODO: Move these uncertainties to the sections where they are applicable.

Emissions Inventories

Using different emissions inventories in a CTM can have large impacts on the simulation. Natural (biogenic or pyrogenic) and human driven (anthropogenic) emissions often drive a large fraction of atmospheric oxidation and radical chemistry, especially in the continental boundary layer. Emissions inventories have been found to be generally OK at larger (regional to global) scales, as long as they are derived from accurate input measurements (Zeng et al. 2015).

It is important to note that many estimates of isoprene emission are based on a few algorithms which can depend greatly on input parameters (Arneth et al. 2008; Niinemets et al. 2010). Arneth et al. (2008) argue that this monopoly of emissions estimates may be leading us to an incorrect understanding of isoprene chemistry. Yue, Unger, and Zheng (2015) has shown that this is still a problem by looking at land carbon fluxes and modelling the sensitivity to VOC emissions estimates using two independent models of VOC emission. One model is photosynthesis based and estimates isoprene emissions using electron transfer energies and leaf physiology (Niinemets et al. 1999), while the other (MEGAN) uses the light and canopy temperature ((Guenther et al. 1995; Arneth et al. 2007) TODO: Read Arneth et al., 2007; Unger et al., 2013). Both are sensitive to light and temperature parameterisations.

Resolution

todo: Yu2016 paper.

GEOS-Chem simulations are somewhat sensitive to the gridbox resolution. For example: Wild and Prather (2006) show that reduced resolution increases OH concentrations and ozone production rates. Christian, Brune, and Mao (2017) find small changes in OH (< 10%) in OH, HO₂ and ozone concentrations local to the north american arctic, when changing from 4 by 5 to 2 by 2.5° resolution.

For many global scale analyses, errors from resolution are less important than those from chemistry, meteorology, and emissions (Christian, Brune, and Mao 2017). Many models lack in-situ measurements with which to verify their chemical mechanisms, leading to large discrepancies, as seen in Marvin2017a TODO: briefly talk about Marvin2017a takeaways.

Chemistry mechanisms

There is still much work to be done in models to correctly simulate emissions and processes which lead to HCHO and ozone. Often HCHO is used as a way of checking if precursors are correctly modelled since HCHO measurements are more readily available (for instance from satellites). GEOS-Chem has recently been analysed for ozone and oxidant (OH and HO₂) sensitivity to the processes within the model along with inputs which drive it (Christian, Brune, and Mao 2017). Christian, Brune, and Mao (2017) found that GEOS-Chem ozone was most sensitive to NO₂ photolysis, the NO₂ + OH reaction rate, and precursor emissions such as VOCs.

Marvin et al. (2017) suggest that isoprene mechanisms in several contemporary models (including GEOS-Chem) are inadequate. They show that for a specific measurement campaign, the HCHO concentrations are underestimated in a way that can

not be easily fixed through rate constant changes. Recently Marvin et al. (2017) compared five global CTMs isoprene mechanisms by evaluating simulated HCHO mixing ratios compared to in situ measurements from the Southeast Nexus (SENEX) aircraft campaign (in southeastern USA). They compared five models (GEOS-Chem, CB05, CB6r2, MCMv3.2, and MCMv3.3.1) and found all of them underestimated the HCHO concentrations (by 15 – 30%).

Another important factor in determining the yield of HCHO and ozone from BVOCs is the local concentration of NO_x . Travis et al. (2016) show how modelled surface ozone is overestimated due to high estimates of NO_x emissions, which affect oxidative capacity and VOC reactions in the US.

Clouds

One of the major uncertainties in chemical, climate, radiation, and weather models is cloud formation and dynamics. Clouds are remarkably complex at a much finer scale than can be accurately modelled by global chemistry models (with current processing power). Globally over half (50-60%) of the world is covered by clouds, with $\sim 10\%$ of them being rain-clouds (Kanakidou et al. 2005). Wet scavenging performed in clouds not only depends on large scale cloud processes, but also on the micro-physics of aerosols being scavenged, differing between aerosol sizes and hygroscopic properties. Cloud filtering is performed on both OMHCHO and OMNO2d products, as those measurements are too uncertain or do not capture enough information. This has been seen to introduce a clear-sky bias - as monthly averages do not include cloudy conditions (Surl, Palmer, and González Abad 2018).

Soil Moisture

Modelled emissions are sensitive to soil moisture, especially near the wilting point, below which trees stop emitting isoprene and other VOCs completely as they can no longer draw water (Bauwens et al. 2016). MEGAN can account for soil moisture by applying it as an emission factor which scales the emission rate of various species. Many environmental parameters are affected by soil moisture, which all play a role at fine scales to surface emissions (Rowntree and Bolton 1983; Chen and Dudhia 2001). Droughts effects can be difficult to measure, as they are a multi-scale problem which affects various aspects of the land-air interface including plant emissions and dry deposition (Wang et al. 2017).

1.6 Australia and the southern hemisphere

Australia has a unique climate, along with soil moisture, clay content and other important properties which affect VOC emissions. These properties are only sparsely measured in Australia due to the spread out distribution of population centres, which make many areas very difficult or expensive to reach. In Australia most long term air quality or composition measurements are performed in or near large cities. Australia is dominated by areas with little anthropogenic influence and few ground based measurements of the natural emissions taking place (VanDerA et al. 2008). Since many

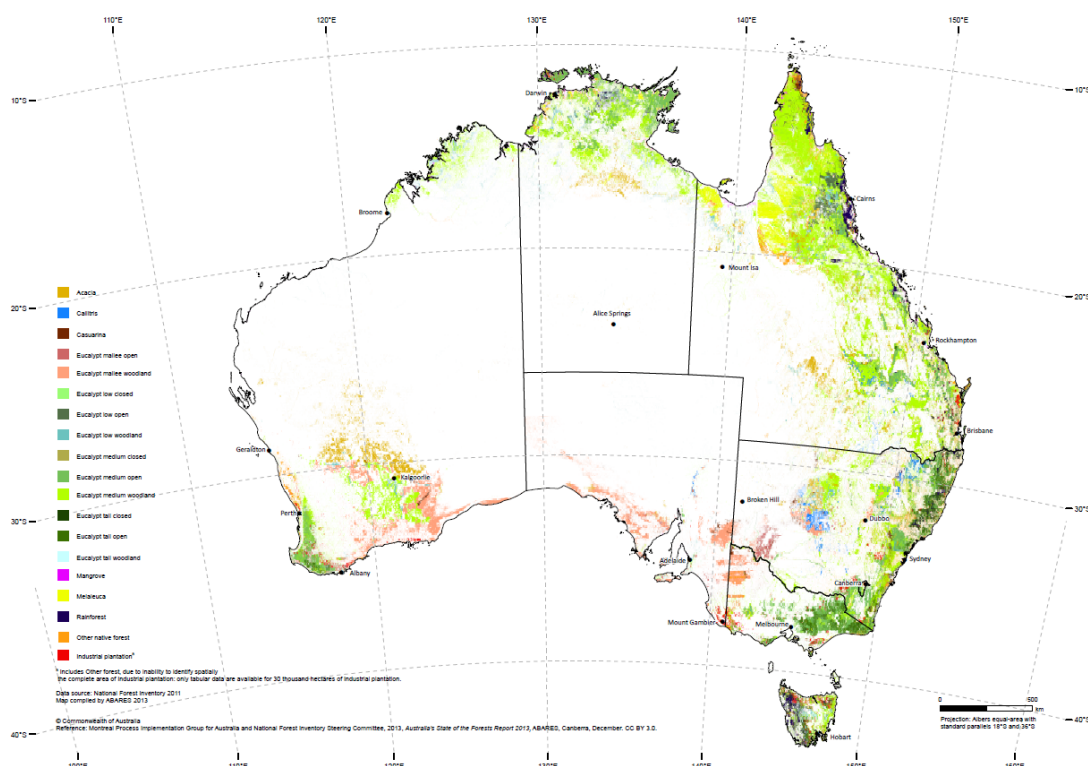


FIGURE 1.11: Forest types in Australia (<http://www.agriculture.gov.au/abares/forestsaustralia/australias-forests>)

Australian cities are on the edge of regions with rich VOC emissions, it is very important to clarify the quantity, type, and cause of VOC emissions. Understanding of emissions from these areas is necessary to inform national policy on air pollution levels.

The vegetation in Australia is diverse, a summary is provided by ABARES using the national forest inventory at <http://www.agriculture.gov.au/abares/forestsaustralia/australias-forests>. Figure 1.11 shows the different forest types and their locations within Australia, highlighting that much of our forested lands are near population centres along the east coast. 16% of Australia is covered by forest, most (75%) of which is Eucalyptus.

Fire emissions include a range of chemical compounds and particulates and each year the effects of fire or burning seasons blanket the northern and southern hemispheres independently. Biomass burning in southern Africa and South America has previously been shown to have a major influence on atmospheric composition in Australia (Oltmans et al. 2001; Gloudemans et al. 2007; Edwards et al. 2006), particularly from July to December (Pak et al. 2003; Liu et al. 2016a).

It has been estimated by MEGAN that the Australian outback is among the worlds' strongest isoprene emitters with forests in SE Australia having emission factors greater than $16 \text{ mg m}^{-2} \text{ h}^{-1}$ (see figure 1.12) (Guenther et al. 2006; Guenther et al. 2012). Measurement campaigns in SE Australia have since cast doubt on the emission factors used by MEGAN, potentially due to poor characterisation of Eucalyptus trees and soil

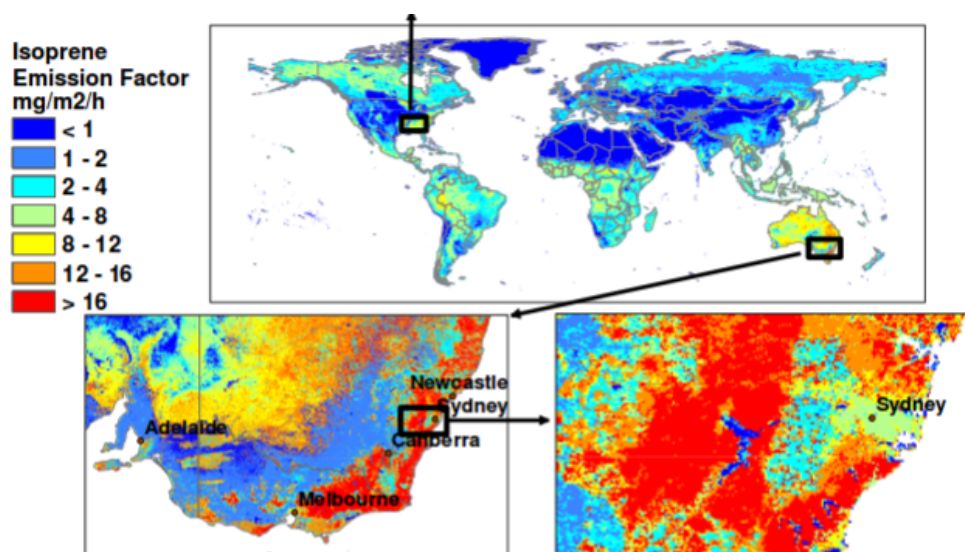


Fig. 2. Global distribution of landscape-average isoprene emission factors (mg isoprene m⁻² h⁻¹). Spatial variability at the base resolution (~1 km) is shown by regional images of the southeastern U.S. and southeastern Australia.

FIGURE 1.12: Part of a figure from Guenther et al. (2006) showing global isoprene emission factors.

moisture (Emmerson et al. 2016). These emissions factor estimates are not well verified and measurements of isoprene (or other BVOC) emissions are sparse and infrequent in Australia (Sindelarova et al. 2014; Bauwens et al. 2016).. In addition, monoterpene emissions are 2-4 times too low, which may be due to underestimated emission rates for many Eucalypt species (Winters et al. 2009; Emmerson et al. 2016).

1.6.1 Ozone

Surface ozone levels over Australia are relatively low (~ 20 ppb) (Young et al. 2017), however it remains unclear how much we would expect this to change in the future as relatively little is known about precursors and influx for the continent. Australian air quality is monitored independently within each state, using several metrics. These metrics are measured by varying numbers of monitoring stations in each state. Measurement stations are generally located in population centres, and don't regularly measure isoprenoid emissions. This is an important omission as these naturally emitted precursor gases often get transported into cities where they affect air quality through production of O₃ and other pollutants.

Generally STT over Australia affects the upper troposphere only, however ozone enhancements can reach quite low during heavy storms and cyclonic weather patterns (Alexander et al. 2013). TODO: More on Australian ozone STT Ozone enhancements over the southern ocean signify either transported pollution or stratospheric influx, due to lack of precursor emissions TODO:cite. Analysis over this region is relatively sparse TODO:cite, and quantification is difficult without large scale extrapolations.

1.6.2 VOCs

Bottom up inventories of VOCs remain largely uncertain due to extensive extrapolation over plant functional types, changing land cover, and parameterised environmental stressors (Guenther et al. 2000; Kanakidou et al. 2005; Millet et al. 2006). Müller et al. (2008) show how isoprene is poorly captured by the MEGAN model and analyse the affect of changing the soil moisture parameter. Sindelarova et al. (2014) show reductions in modelled Australian isoprene emissions of 50% when incorporating soil moisture in MEGAN estimates. Uncertainties in isoprene emissions could explain why models of HCHO over Australia are poor at reproducing satellite measurements (Stavrakou et al. 2009).

Australia suffers from poor characterisation of plant emissions, partly because emission factors are based on northern hemispheric data. Many plant emissions rates have not been published, such as those for any Australian acacias. Some Eucalypt emissions are based on samples from young trees, which may emit more isoprene than older trees (Emmerson et al. 2016). Additionally soil moisture is not well quantified which has a large effect on emissions. Soil type and moisture, along with drought thresholds, have poorly understood effects on plant emissions in Australia. Changes in parameterisation of soil moisture in the MEGAN lead to massive changes in Australian isoprene emission estimates (Sindelarova et al. 2014). Over Australia MEGAN suffers from a lack of studied plant functional types and their emissions (eg. Müller et al. 2008). Emission rates from various species of eucalypt and other flora are highly complex, depending on current and recent weather, temperature, tree age, health, etc. (Guenther et al. 2012). With this complexity added to the diversity of tree species in Australia as well as sparse rural data collections it is hard to model and verify emissions.

Emmerson et al. (2016) analysed isoprene and monoterpene emissions sensitivities in a regional model of atmospheric chemistry over southeast Australia, using four campaigns which are also examined in this thesis. They show that modelled emissions require spatially and temporally resolved changes. Emmerson et al. (2016) suggest that monoterpenes may be emitted in similar quantities to isoprene, with more measurements required to determine if this is so. They compare emissions estimates from MEGAN against field campaign data and see overestimated isoprene emissions, as well as underestimated monoterpene emissions. Their work suggests that MEGAN estimates of isoprene emissions may be 2-6 times too high, and monoterpene emissions ~ 3 times too low over southeast Australia.

Improvements to emissions models require improved understanding of regions and their behaviour. Satellite measurements can be used to improve understanding of Australian emissions. As HCHO is produced with relatively high yield after isoprene is emitted, we can use satellite measurements to estimate isoprene emissions (Palmer et al. 2001; Millet et al. 2006; Bauwens et al. 2016, e.g.).

1.6.3 Measurements

TODO: Brief overview of all the measurement campaigns, pointing to Modelling and Data chapter for more details. There are relatively few measurements of isoprene in the southern hemisphere, including MUMBA(TODO CITE), SPSS(cite), Tumbarumba

(Emmerson et al. 2016), and that girl from Macquarie University with an instrument in the daintree rainforest(TODO CITE, DESCRIBE). For details on the MUMBA campaign see Section 2.2.2. An airflight campaign (HIPPO) measuring isoprene was also performed in 2009-2011? TODO: ask Jenny re this one.

A particulate and air quality measurement campaign took place in Sydney using PTR-MS and GC-FID, for details see Section 2.2.3.

One method of measuring ozone in the troposphere and stratosphere is by releasing weather balloons (with attached ozone detectors) which take readings as they rise up to around 30 km, giving a vertical profile of concentrations. Since 1986, Lauder, New Zealand (45°S, 170°E) has released ozonesondes allowing a multi-decadal analysis of ozone concentrations over the city (Brinksmas et al. 2002). Kerguelan Island (49.2°S, 70.1°E), also has a record of ozonesonde profiles, which are directly in the path of biomass burning smoke plumes transported off shore from Africa (Baray et al. 2012). SHADOZ is the southern hemispheric additional ozone project, which have released sondes from 15 sites at different times <http://tropo.gsfc.nasa.gov/shadoz/>.

A smaller network of ozonesonde release sites is operated by TODO: get details for sondes I use in ozone chapter.

1.7 Aims

In this thesis I aim to improve understanding of natural contributions to ozone over Australia and the southern ocean. The two largest contributors to tropospheric ozone concentrations are chemical production (driven by precursor emissions) and stratospheric transport. I aim to improve understanding of both of these sources using existing satellite and ground-based datasets along with GEOS-Chem modelled outputs.

Calculation of isoprene to HCHO yields over Australia is required to create top-down estimates. This requires among other things an idea of which VOCs are present and their yields of HCHO. The technique of determining isoprene emissions from satellite detected HCHO is called satellite inversion. **I aim to determine isoprene to HCHO yield over Australia, and the importance of relevant parameters using GEOS-Chem.** This includes an examination of how well GEOS-Chem simulates several species such as NO_x, isoprene, and HCHO compared to campaign and satellite data that exists for Australia. TODO: summary of stuff in modelling chapter. Work to complete this aim is in Chapter 2.

One of the aims in this thesis is to use available satellite measurements to improve the estimates of isoprene emissions in Australia. Satellites which overpass daily record reflected solar (and emitted terrestrial) radiation, and give us measurements over all of Australia. Combining satellite data with model outcomes provides a platform for the understanding of natural processes which is especially useful over Australia. Due to the low availability of in-situ data over most of the Australian continent, a combination of the models with satellite can fill the gap of understanding of emissions from Australian landscapes. Improved emissions estimates will in turn improve the accuracy of CTMs, providing better predictions of atmospheric composition and its response to ongoing environmental change. The work done to complete this aim is in Chapter 3.

To improve understanding of ozone transported to the troposphere from the stratosphere in Australia and the southern ocean. Stratospheric transport is the second largest driver of tropospheric ozone concentrations, and an improved understanding of transported ozone can be determined from ozonesonde measurements. Ozonesondes provide a glimpse of the vertical ozone profile up to ~ 30 km, and we use a Fourier filter to determine how often stratospheric transport is occurring at three sites: Melbourne, Macquarie Island, and Davis Station. Combining transport event frequency analysis with modelled ozone distributions is used to derive a new method of detection and quantification of transported ozone in Chapter 4.

TODO: conclusions chapter aims? **I aim to describe relative importance of sources of tropospheric ozone in Australia, as well as seasonality.**

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